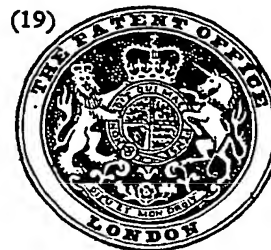


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(54) PROCESS FOR THE PREPARATION OF GRANULAR OR
 POWDERY POLYAMIDE

(71) We, STAMICARBON N.V., a Netherlands Limited Liability Company of 2 van der Maesenstraat, Heerlen, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of particulate polyamide, e.g. in the form of granules or powders, of the type comprising the anionic catalytic solution polymerization of at least one lactam containing at least 6 ring carbon atoms at a temperature below the melting point of the polyamide to be formed, to particulate polyamides produced by such a process, and to shaped artefacts formed wholly or partly from such polyamides.

It is difficult for reproducible results to be achieved by such a known process. Thus it is difficult to control the product grain size, the degree of polymerization and the polymerization rate, whilst the yield is small and the resulting polyamide in many instances forms lumps, settles on the reactor wall and the stirrer and is separable from the solvent with difficulty.

In order to overcome these difficulties it has previously been proposed in Patent No. 1,118,700 for the catalyst and/or the promoter to be added in small increments to the dissolved monomer or for the polymerization to be carried out in the presence of a high molecular weight polymer which serves to refrain the newly formed polyamide particles from agglomerating, or in Patent No. 1,058,492 for a solvent to be used having a specific gravity which lies between the specific gravities of the lactam monomer and the polyamide to be formed.

The present invention is directed to a process wherein without the necessity of taking special precautions a powdered or granular polyamide may be obtained by anionic

catalytic polymerization of lactams without the attendance of the difficulties hereinbefore described.

The invention provides a process for the preparation of particulate polyamide comprising polymerizing at least one lactam containing at least 6 ring carbon atoms in a solution thereof in an inert solvent for the lactam but which is a non-solvent for the polyamide product at a temperature below the melting point of the polyamide to be formed, the polymerization being effected in the presence of an anionic polymerization catalyst and of bis-ε-caprolactimether as promoter. The use of bis-ε-caprolactimether as promoter for anionic polymerisation is the subject of our prior Specification No. 1,022,669.

By the process according to the invention, a polyamide is formed in good yields, which can readily be separated from the solvent used, and which has a narrowly-distributed grain-size distribution. The density of the polyamide thus obtained is higher than has hitherto been obtained, and contains a low proportion of material which may be extracted with water.

The weight-average molecular weight of polyamides obtained according to the invention generally is between 20,000 and 100,000, although higher values may be obtained.

Polymers obtained according to the invention may readily be spun and extruded even though the relative viscosity is high. For instance, a polyamide having a relative viscosity of 4.0 can readily be spun, whereas a polyamide having a relative viscosity of 3.0 prepared by hydrolytic polymerization can be spun only with difficulty. Polyamides obtained according to the invention also may readily be coloured.

The mechanical properties of polyamides prepared according to the invention compare favourably with those of polyamides prepared in the presence of other promoters. Thus the notch impact strength is high with a high E-

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particles, see page 3

modulus, whereas with polyamides conventionally obtained an increase in impact strength is usually only obtained at the expense of the E-modulus. The creep value of extruded products obtained according to the invention is low, the bending strength and the yield value being high.

The bis- ϵ -caprolactimether promoter used according to the invention may be in either one of the two tautomeric forms thereof. The said promoter may be used in a proportion of from 0.1 to 5.0, preferably 0.5 to 2.0 mol. %, based on the lactam monomer. A particular advantage of the use of the promoter according to the invention is that the molar ratio between catalyst and promoter is not critical. Thus when using other promoters the said ratio should be 1 or more, as a lower ratio affects the polymerization reaction. When bis- ϵ -caprolactimether is used as promoter the ratio may either be larger or smaller than 1 without detriment to the polymerization reaction. Preferably a catalyst/promoter molar ratio of between 4:1 and 1:4 is used in the process according to the invention.

Catalysts which may be used in the process of the invention include metal-lactams or substances capable of reacting with lactam to form a lactam-anion. Examples of such catalysts include alkali-metal lactams; alkali metals; alkaline-earth oxides, hydroxides, alkoxides and hydrides and Grignard compounds. The catalyst may be used in a proportion of from 0.1 to 5.0 generally from 0.5 to 2.0 mol.-% based on lactam monomer feed. The catalyst may be added directly to a solution of the lactam feed, or may be pre-reacted with a proportion of molten lactam, the resulting volatile by-products being removed and the lactam-anion-containing melt added to the solvent.

The polymerization reaction should be carried out with stirring to keep the reactants homogeneously distributed. Thus the stirring may be effected at a rate of from 200 to 800 revolutions per minute.

To obtain a reasonable rate of polymerization the polymerization temperature is below the melting point of the polyamide product, but preferably higher than 100°C, preferably between 125 and 170°C. In this temperature range the polymerization proceeds rapidly with simultaneous crystallization and particle growth of polyamide particles previously formed.

The polymerization is effected in at least one inert solvent for the lactam feed at polymerization temperature and in which the polyamide product is not substantially soluble under polymerization conditions. Particular examples include toluene, xylenes, gasoline having a boiling range of from 80 to 140°C, tetramethylpentane, pentamethylheptane and tetralin. Preferred solvents are those having a boiling point which lies near or above the

polymerization temperature, so that it is not necessary to work at a superatmospheric pressure. In order to avoid disturbing of the polymerization and the formation of coloured product, the reaction polymerization is preferably effected with the exclusion of water and oxygen.

As monomer feeds lactams and mixtures of lactams having at least 6 ring carbon atoms may be used, particular examples including caprolactam, oenantholactam, capryllactam, lauro lactam, substituted lactams and lactams having an ether- or thio-ether bridge in the ring. Particularly preferred are ϵ -caprolactam and lactam mixtures containing ϵ -caprolactam.

After polymerization has been completed the resulting powdery or granular polyamide may readily be separated from the solvent in a conventional manner, and if necessary the catalyst residues may be removed by washing the material with hot or cold water and/or with an alcohol, or by steaming. The catalyst residues may readily be removed as they are located substantially only at the surface of the polyamide particles.

The invention may be applied to a process for the preparation of polyamide particles containing fillers by effecting the polymerization as hereinbefore described according to the invention in the presence of a filler.

In processing filler-containing polyamides into for instance, moulded artefacts or coating layers, particles of filled polyamide using conventional techniques including for example injection-moulding, compression and whirling-sintering may be used. Such particles may be obtained by processing a mass of polyamide produced by bulk-polymerization or by anionic polymerization in situ, in which particles of the filler have been distributed for instance by grating or grinding. Such a process however is unwieldy and results in particles which are irregular in shape and size. Previously-proposed processes for preparing a filler-containing particulate polyamide in one step comprises anionically polymerizing a lactam which is dissolved in a solvent, in which solvent a filler is distributed. Such a process is described and claimed in Specification No. 1,211,083.

It is also previously known that the anionic solution polymerization of a lactam can be carried out in the presence of dispersing agents that are not soluble in the reaction medium. The dispersing agent may however become trapped in an envelope of the polyamide formed, which is generally undesirable.

The process according to the present invention may be used to provide a particulate filled polyamide in one step, without any limitations of the type hereinbefore described on nature and quantity of the filler. Thus in the anionic polymerization of one or more lactams dissolved in an inert solvent using according to the invention bis- ϵ -caprolactimether as pro-

motor and at a temperature below the melting point of the polyamide to be formed, one or more fillers are distributed in the reaction medium before or during the polymerization reaction.

By this means each filler particle is coated with a thin layer of polyamide to provide a particulate filled polyamide. No agglomeration of polyamide particles or polyamide growth on the reactor wall occurs, and the filler need not have any dispersing effect. The adherence of the polyamide to the filler is good and the quality of the filled polyamide thus formed is excellent.

A wide variety of fillers may be used, providing they possess no substantial solubility in the solvent used in the polymerization and do not interfere with the polymerization reaction. It is desirable for the filler to be used in the dry state, as water has a disturbing effect. If necessary the surface of the filler can be treated so as to become deactivated before incorporation in the polymerization medium. If desired an adhesion agent may be provided for enhancing the adhesion of the polyamide to the filler surface.

Organic or inorganic fillers may be used, particular examples including powdered or fibrous metals e.g. iron, copper, nickel, titanium, vanadium, chromium, cobalt or aluminium; boron; minerals e.g. quartz, feldspar, asbestos, mica, dolomite, graphite, talc and cristobalite; oxides e.g. boron oxide, aluminium oxide, titanium oxides and magnesium oxide; carbides; borides; silicates; carborundum; glass fibres; glass wool, carbon materials, e.g. carbon black or carbon fibres; inorganic pigments; thermo-set resins e.g. phenol-formaldehyde resin; thermoplastic synthetic materials which do not soften to a great extent under the polymerization conditions e.g. polyamides or polytetrafluoroethylene.

Glass fibres and carbon fibres are particularly preferred filler materials.

The filler particles may differ in shape, although they are preferably of uniform shape. Thus the particles may be spherical having a diameter between 10 Å and 1 cm, the particles preferably being of a uniform size as possible. Cylindrical or fibrous particles may be used, having a diameter between 0.5 microns and 100 microns and length between 5 microns and 2 cm. The length/diameter ratio may be for example from 20,000:1 to 5:1. If fibrous fillers are used, the length/diameter ratio is preferably between 2,000:1 and 10:1. A polyamide powder that can be processed into objects or coating layers having good physical properties, is obtained by using a mixture of a fibrous and a powdery filler. Examples of such combinations include as fibrous filler glass fibre, carbon fibre, asbestos fibre or metal fibre, and as powdery filler powdered carbon black, quartz, talc, granite, slate or graphite.

If desired mixtures of either powdery or fibrous fillers may be used. If under the polymerization conditions the filler shows a tendency to soften, dissolve or otherwise degrade, the polymerization reaction may with advantage be initiated in the absence of the filler, the filler subsequently being added as soon as the polymerization mixture displays a slight turbidity.

The quantity of filler which is added should not exceed the amount that may be maintained in a dispersed condition in the solvent. Of course the amount of monomer present when the polymerization is initiated should be sufficient for the total surface of the filler contained in the solution to be coated with a polyamide layer of required thickness. Such an upper limit is approximately a filler surface of 20 m² per gramme of monomer. There is no lower limit for the quantity of filler which may be added.

The following Examples of the invention are provided, together with Comparative Experiments wherein polymerization has been effected using other promoters, e.g. acetyl caprolactam and benzoyl chloride.

In the Examples the relative viscosity was determined at 20°C in solutions of 1.0 g of polymer in 100 mls. of sulphuric acid.

Example I

200 g of dry caprolactam were melted under a nitrogen atmosphere at a temperature of 90°C in a 1 litre glass reactor. Subsequently sodium hydride as catalyst was added, and after the evolution of hydrogen ceased, 0.4 litre of dry pentamethylheptane was added and the solution heated to the desired temperature. Bis-ε-caprolactimether was then added as promoter. After a period of time the solution turned opaque due to the formation of small solid polyamide particles. Microscopic examination of particles removed at intervals from the solution showed that the particles progressively grew in size to form spherulites of regular shape.

Upon completion of the polymerization, the polyamide product was filtered off, washed with water and dried.

The yield was determined as a percentage of the theoretical yield, and the specific density, percentage of material extractable with water (WOE) and the relative viscosity both before and after an extraction, were also determined.

Powdery polyamides were prepared using different catalyst/promoter ratios, polymerization times and polymerization temperatures. The results are summarized in Table 1, runs 1 to 4.

For comparison with Example I polyamides were prepared in similar manner, but using acetyl caprolactam and benzoyl chloride as promoters. The results are also shown in Table 1, runs 5 and 6, and 7 and 8 respec-

tively. Polyamides obtained by polymerization using these promoters have a low relative viscosity and are formed in low yields, and furthermore the grains are more irregular in form and tend to agglomerate.

5

TABLE I

Run	catalyst NaH mol.-%	promoter mol.-%	time hours	temp. °C	yield %	WOE %	η rel. before extr.	after extr.	density g/ml
1	0.5	1.0B	7	145	64	0.6	3.79	3.93	1.174
2	0.5	0.5B	6	150	64	<0.2	—	7.0	1.172
3	0.5	0.5B	18	145	92	0.6	7.90	7.5	1.176
4	0.5	0.5B	11	140	92	0.4	6.88	6.5	1.172
5*	0.5	0.5A	1	160	39	1.4	2.68	2.74	—
6*	0.5	0.5A	6	130	34	0.9	2.64	2.53	—
7*	1.5	1.0C	1	140	43	3.2	1.63	1.63	—
8*	0.75	0.25C	4	140	20	1.2	3.19	2.78	—

* not according to the invention

B = bis- ϵ -caprolactimether

A = acetyl lactam

C = benzoyl chloride

Example II

Polyamides were prepared in the manner described in Example I, except that the preparations were on a pilot-plant, using a minimum of 30 kg of caprolactam in 60 litres of pentamethylheptane, in a 140 litre reactor provided with a turbine-stirrer. The stirring speed was 500 rpm. The results are shown in Table 2, runs 9 to 14.

For comparison, polyamides were prepared in the manner described in Example II, except that acetyl caprolactam and benzoyl chloride were used as promoters. The results are shown in Table 2, runs 15 and 16 respectively. In run 11, a temperature runaway was experienced, as shown in the short reaction time.

TABLE 2

Run	catalyst NaH mol.-%	promoter mol.-%	time hours	temp. °C	yield %	WOE %	η rel. before extr.	η rel. after extr.
9	0.5	1.0B	10	142-145	87	0.4	4.63	4.46
10	0.5	0.5B	10.5	140-147	70	0.4	5.58	5.45
11	0.5	1.5B	2.5	140-170	70	0.4	5.43	5.53
12	0.5	0.5B	17	135-145	83	0.8	6.87	6.40
13	1.5	0.5B	7	140	67	1.2	5.43	4.97
14	1.0	1.5B	9	135-145	92	0.1	3.63	3.81
15	0.5	0.5A*	17	130	30	0.4	2.80	2.80
16	0.75	0.25C*	5	145	14	0.6	2.37	2.29

* not according to the invention

B = bis- ϵ -caprolactimether

A = acetyl caprolactam

C = benzoyl chloride

Example III

The grain-size distribution of the polyamides prepared in runs 9 to 13 was determined by screening the material into different fractions. The results are shown in Table 3 under runs nos. 9—13.

The grain-size distribution of the poly-

amides prepared in runs 15 and 16 was determined, and the results are shown under nos. 15 and 16 in Table 3. Thus the polyamides prepared with the aid of acetyl caprolactam and benzoyl chloride as promoters, respectively, show a wide grain-size distribution.

TABLE 3

Run	<33 μ %	33—40 μ %	40—65 μ %	65—75 μ %	90—120 μ %	
9	9	48	38			
10	6	31	55			
11	2	4	1		71	11%>120 μ
12	3	1	57	37		
13	1	50	45			
15*	22	19	19	9	16	11%>120 μ
16*	0	2	2	10	4	76%>180 μ

* Not according to the invention

From the polyamides prepared in runs 9 to 13, small specimen plates were made by injection moulding. The said plates were used to determine the E-modulus and the breaking strength, and the notch impact strength (Izod value), both before and after conditioning. The relative viscosity of the polyamide was again determined after the processing, and the results are shown in Table 4 under Nos. 9—13.

A small specimen plate was made of the polyamide obtained in run 15, and several properties determined. The results are shown in Table 4 under no. 15. All properties, with the exception of the E-modulus, are inferior to those of the polyamide prepared according to the invention.

TABLE 4

Run no.	E-modulus kg/cm ²	breaking strength kg/cm ²	η rel.	before	Izod kg/cm ² after conditioning
9	9600	481	4.8	5.7	n.b.*)
10	9050	534	6.0	6.1	n.b.
11	9660	556	7.4	5.6	n.b.
12	9770	603	8.2	4.7	n.b.
13	8920	564	4.7	5.6	n.b.
15 ¹⁾	11030	410	2.7	4.5	37

*) No breakage under test conditions

¹⁾ Material obtained in process not according to the invention

Example IV

A mixture of 400 ml of pentamethyl heptane, 200 g of ϵ -caprolactam and 0.133 g of sodium hydride (0.5 mol.-%) as catalyst was heated to 120°C with stirring. The solution thereby formed was successively supplied with 2 g of powdery titanium dioxide of average grain size 2 microns as filler material and 1.91 g of bis- ϵ -caprolactimether (0.5 mol.-%) as promoter according to the invention, and the temperature brought to 45°C. The reaction mixture was stirred for 12 hours at a temperature of 145°C, and the polyamide powder formed filtered off and washed with water. 172 g of filled polyamide powder were obtained containing 1.1 % by weight of titanium dioxide.

Example V

Using the method used in Example IV, a solution of 200 g of caprolactam in 400 ml of decalin was polymerized with the aid of

1.0 mol.-% of NaH as catalyst and 1.0 mol.-% of bis- ϵ -caprolactimether as promoter according to the invention, in the presence of 20 g of ground glass fibres as filler material. The polymerization was effected at 150°C for a period of 8 hours. 198 g of polyamide powder were obtained containing 10% by weight of glass fibres.

Example VI

Using the method used in Example IV, powdery polyamides containing as fillers iron, carbon black, ground glass wool, glass fibres and carbon fibres, were prepared by polymerizing 200 g of caprolactam dissolved in 400 ml of pentamethyl heptane, with the aid of 1.0 mol.-% of NaH as catalyst and 1.0 mol.-% of bis- ϵ -caprolactimether as promoter according to the invention. The average dimensions of the filler particles were as follows:

iron	diameter 10 microns
carbon black	diameter 20 millimicrons
glass fibre	diameter 10 microns, length 100 μ
carbon fibre	diameter 10 microns, length 500 μ

The polymerization conditions and the results are shown in Table 5.

In all instances the filler material was

incorporated in the polyamide particles without the formation of deposits on the reactor wall or agglomeration of the polyamide particles.

TABLE 5

Run	filler used	temp. °C	yield after extraction g	% by w. of filler in product	η rel.
1	20 g of glass wool, ground	150	204	9.8	—
2	20 g of glass fibres, ground	150	208	9.6	—
3	50 g of glass fibres, ground	150	185	27.0	—
4	10 g of carbon fibres, ground	150	142	7.0	—
5	5 g of carbon black	160	194	2.5	—
6	1.0 g of iron carbonyl	145	173	0.6	4.3
7	1.0 g of iron in emulsion*)	145	187	0.5	5.3
8	5.0 g of iron in emulsion	145	183	0.9	5.8
9	40 g of iron carbonyl	160	200	20	—

*) The emulsion consisted of 75 g of finely dispersed iron particles of average diameter of 10 μ , 30 g of caprolactam, 60 g of pentamethyl heptane and 1.0 g of a non-ionic dispersing agent obtained under the Trade Mark GAFAC RE 160, sold by the General Aniline and Film Corporation of Linden, N.J., U.S.A.

5 The polyamides obtained in Example V were processed into test bars and small test plates and the physical properties of the materials determined after the material had been conditioned by being kept for 8 days in an atmosphere of relative humidity of 65% and a temperature of 70°C. The E-modulus and flexural strength were determined by

means of a flexural test according to ASTM Standard D-790 procedure. The breaking load, elongation and the yield point were determined by means of a tensile test, the notch impact strength (Izod value) being determined according to ASTM Standard D-256-56 procedure. The results are summarized in Table 6. 10 15

TABLE 6

filler % by w.	E-modulus kg/cm ²	flexural strength kg/cm ²	elongation %	yield point kg/cm ²	breaking load	Izod kg/cm ²
9.8 glass wool	23,100	715	140	490	440	9.8
9.6 glass fibres	26,100	754	155	496	494	10.8
27.0 glass fibres	38,400	875	39	520	445	6.7
7.0 carbon fibres	29,000	870	29	617	—	10.4
2.5 carbon black	15,200	533	140	497	523	8.9
0.6 iron carbonyl	13,300	477	213	492	330	31.8
0.5 iron	13,400	463	180	480	518	27.8
0.9 iron	14,000	460	217	492	614	25.3

20 The physical properties of filled polyamides prepared in Example IX, were determined in the unconditioned state in the form of small test plates and bars. By way of com-

parison, the properties of a non-filled polyamide, prepared in a way analogous to Example IV, were determined. The results are shown in Table 7. 25

TABLE 7

filler % by w.	E-modulus kg/cm ²	flexural strength kg/cm ²	elongation %	yield point kg/cm ²	breaking load	Izod kg/cm ²
27 glass fibres	57,400	1448	<2	—	859	4.4
7 carbon fibres	47,300	1590	<2	—	840	4.0
0.9 iron	35,200	1250	60	741	577	6.0
—	33,200	1230	150	770	650	6.2

Example VII

30 In the manner described in Example IV, a solution of 180 g of caprolactam in 400 ml of pentamethyl heptane was polymerized with the aid of 1.0 mol.-% of NaH as catalyst and 1.0 mol.-% of bis-ε-caprolactimether as promoter according to the invention in the presence of 9 g of iron carbonyl and 9 g of ground glass fibres. After a polymerization

time of 9 hours at 150°C, 141 g of polyamide powder were obtained consisting of a mixture of iron-containing polyamide particles and polyamide particles containing glass fibres.

WHAT WE CLAIM IS:—

40 1. A process for the preparation of particulate polyamide comprising polymerizing at least one lactam containing at least 6 ring carbon atoms in a solution thereof in an inert

5 solvent for the lactam but which is a non-solvent for the polyamide product at a temperature below the melting point of the polyamide to be formed, the polymerization being effected in the presence of an anionic polymerization catalyst and of bis-ε-caprolactimether as promoter.

10 2. A process according to Claim 1, wherein the said bis-ε-caprolactimether is present in a proportion of from 0.5 to 2 mol. %, based on the lactam monomer.

15 3. A process according to Claim 1 or Claim 2, in which the polymerization is effected at a temperature between 125°C and 170°C.

4. A process according to any of Claims 1 to 3, in which one or more fillers are dispersed in the reaction mixture prior to or during the polymerization.

20 5. A process according to Claim 4, in which the filler is a fibrous filler having a length/diameter ratio between 2000:1 and 10:1.

6. A process according to Claim 4 or Claim 5, in which a mixture of a fibrous and

a powder filler is dispersed in the said reaction mixture.

7. A process according to any of Claims 4 to 6, in which glass fibres are dispersed in the said reaction mixture as filler.

8. A process according to any of Claims 4 to 7, in which carbon fibres are dispersed in the said reaction mixture as filler.

9. A process according to any of Claims 1 to 8, in which the lactam monomer is caprolactam or a caprolactam-containing mixture of lactams.

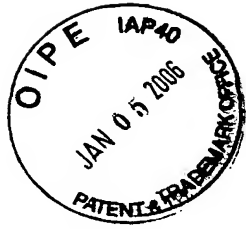
10. A process for the preparation of a particulate polyamide as claimed in Claim 1, substantially as hereinbefore described.

11. Particulate polyamide prepared by the process according to any of Claims 1 to 10.

12. Shaped artefacts, made wholly or partly of a polyamide according to Claim 11.

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